DECON GREEN, THE ENVIRONMENTALLY-FRIENDLY DECONTAMINANT

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ABSTRACT

A simple solution of hydrogen peroxide, potassium carbonate, potassium molybdate, propylene carbonate and Triton® X-100 (a non-ionic surfactant) affords the rapid, broad-spectrum decontamination of chemical warfare agents, even at low temperatures (–30 °C). The solution is non-corrosive, environmentally-friendly, and leaves no toxic residues. This novel decontaminant has been appropriately named Decon Green. In situ generation of peroxy anion OOH^- effects perhydrolysis of nerve agents such as VX and GD to yield non-toxic products. For HD, in situ-generated peroxo species afford oxidation, initially, to the non-vesicant sulfoxide. Decon Green is superior to other common decontaminants for the decontamination of painted surfaces of military interest.

INTRODUCTION

The U.S. Army is developing environmentally friendly decontamination systems to replace current, problematic decontaminants such as hypochlorite and others.[1] Desirable characteristics for the replacement include maintaining a broad-spectrum reactivity towards all agents, even in cold weather operations, while achieving a significant reduction in the corrosive and environmentally harmful nature of the decontaminant. Current decontaminants are corrosive and, furthermore, can produce undesirable products. Some of these side-reaction products retain toxic, irritant and/or vesicant properties.[1,2]

In industrial applications, environmental concerns have been driving the replacement of chlorine-based bleaching processes with peroxide-based systems.[3] These "green" peroxide strategies avoid the formation of toxic, carcinogenic chlorinated organic compounds such as those generated in paper production.[4] This work demonstrates that a peroxide-based system may also be employed in *military* applications, replacing historical chlorine-based "bleach" decontaminants and others.[1] Such a system affords the necessary rapid reactions and, as in the case of industrial bleaching, avoids undesirable products. This peroxide-based decontaminant has been appropriately named "DECON GREEN."[5]

Another advantage of peroxides is evident for the development of cold-weather decontamination solutions: the freezing points of 50% and 35% aqueous hydrogen peroxide (H_2O_2) solutions are –55 and –33 ºC, respectively. Indeed, solutions formulated with 50% H_2O_2 do not freeze, phase separate, or precipitate activators down to at least –50 ºC. Although formulations employing 50% H_2O_2 afford significantly greater reactivity than 35% H_2O_2, the former cannot be shipped commercially by air, whereas the latter can. Thus 35% H_2O_2 is perhaps more convenient for use in the field, and most of the data reported below is for the formula using this material.

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RESULTS AND DISCUSSION

Basic peroxide has been known to rapidly decontaminate GB, **1**, for decades,[6] via generation of the powerful nucleophile peroxy anion, OOH^{-}. This reaction is shown in Scheme 1. The K_2CO_3 component generates OOH^{-} in Decon Green. Neutralization levels for GD at various temperatures are shown in Table 1.

Scheme 1

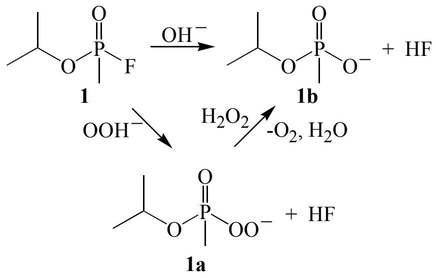


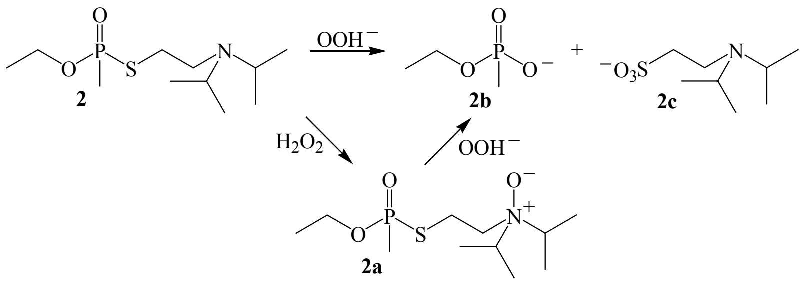
Table 1. VX, GD, and HD Reactivity[a] in Decon Green[b]

Temperature	VX	GD	HD
25ºC	81%	>99.8%	>99.0%
–31ºC	29.2%	55%	3.5%
+49ºC	>86.9%	>99.8%	>99.0%

[a]15 min. neutralization; 0.1M agent challenge.
[b]60 vol % propylene carbonate; 30 vol % 35% H_2O_2; 10 vol % Triton® X-100; 0.15 M K_2CO_3; and 0.02 M K_2MoO_4.

Quite recently it was found that VX, **2**, also undergoes rapid perhydrolysis[7] to yield selectively ethyl methylphosphonic acid (EMPA), **2b**, as shown in Scheme 2. The *N*-oxide of VX, **2a**, also forms and similarly undergoes perhydrolysis but at a slower rate. Perhydrolysis is a much more effective decontamination reaction for VX than basic hydrolysis since toxic EA-2192 is avoided, whereas basic hydrolysis yields about 22% EA-2192.[8] Neutralization levels for VX are shown in Table 1.

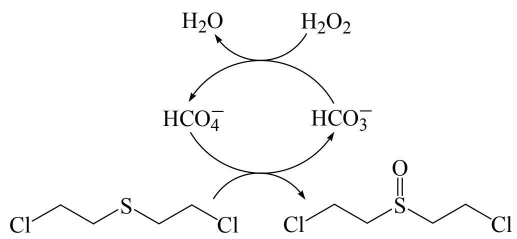
Scheme 2



Although HD, **3**, can be decontaminated by hydrolysis to non-toxic thiodiglycol,[1] its nucleophilic substitution is quite slow. On the other hand, the oxidation of HD to the sulfoxide, **3a**, and sulfone can be extremely rapid.[1,9] Regarding the suitability of the sulfoxide and sulfone as decontamination products, the former is nonvesicant and quite stable to hydrolysis, whereas the sulfone still retains appreciable vesicant activity, although it is prone to hydrolysis.[10-12] Thus, HD can be rendered nonvesicant via selective oxidation to the sulfoxide. If formed, however, the sulfone is water soluble and thus more amenable to hydrolysis than HD itself. Non-activated H_2O_2 selectively oxidizes HD to the sulfoxide, but the reaction is too slow for purposes of immediate decontamination. However, the K_2CO_3 and K_2MoO_4 components of Decon Green (see Footnote B, Table 1) function as activators for H_2O_2, generating the peroxo species HCO_4^{-} and $Mo(OO)_4^{2-}$, respectively.[13-16] These species selectively oxidize HD to the sulfoxide at a much faster rate than H_2O_2, with

$Mo(OO)_4^{2-}$ affording the oxidation about two orders of magnitude faster than HCO_4^- (thus its inclusion in the formula).[13,16] Neutralization levels for HD are shown in Table 1.

Scheme 3



3 **3a**

In addition to fast neutralization of agents in solution, Decon Green also decontaminates agents on surfaces. Table 2 shows that Decon Green is superior to DS2 for the decontamination of CARC painted panels. Note that like DS2, Decon Green is very adept at quickly dissolving thickened agents as shown for thickened GD (TGD). Table 3 further shows that, in the absence of surface sorption effects, Decon Green neutralizes agents to very low levels within 15 min.

Table 2. Decontamination of CARC Panels[a]

Decontaminant	VX	TGD	HD
Decon Green[b]	86.5%	98.0%	90.0%
DS2	72.1%	96.4%	86.7%

[a]10 g/m^2 agent challenge; 30 min. neutralization. [b]Formulated with 50% H_2O_2.

Table 3. Surface Contact Hazard Test[a]

	VX	GD	HD
Decon Green[b]	>99.98%	>99.98%	>99.994%
Water Rinse	99.92%	99.76%	80.25%

[a]10 g/m^2 agent challenge on filter paper; 15 min. neutralization. [b]Formulated with 35% H_2O_2.

In addition to its effectiveness against chemical agents, Decon Green is also extremely efficacious against bio agents. Table 4 shows that Decon Green reduces *Bacillus anthracis* (Anthrax) to undetectable levels within 10 min.

Table 4. Anthrax Spore Destruction[a,b]

Residual Spores	Log Kill
< 10 (none detected)	> 7

[a]7×10^7 spore challenge; 10 min. neutralization.
[b]Formulated with 35% H_2O_2.

CONCLUSIONS

Decon Green is a rapid, effective decontaminant for VX, GD, HD, and thickened agents, and is also extremely effective against anthrax. Decon Green is superior to the current decontaminant DS2 for the decontamination of CARC painted surfaces. The environmentally friendly components of Decon Green (60 vol % propylene carbonate, 30 vol % 35% H_2O_2, 10 vol % Triton® X-100, 0.15 M K_2CO_3, and 0.02 M K_2MoO_4) leave no persistent toxic residues; thus alleviating the usual concerns of decontaminant containment, cleanup and disposal.

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REFERENCES

1. Yang, Y.-C.; Baker, J. A.; Ward, J. R. *Chem. Rev*. **1992**, *92*, 1729-1743.
2. Davis, G. T.; Block, F.; Sommer, H. Z.; Epstein, J. *Studies on the Destruction of Toxic Chemical Agents VX and HD by the All Purpose Decontaminants DS-2 and CD-1*, EC-TR-75024; U. S. Army Edgewood Research Development and Engineering Center, 1975 (UNCLASSIFIED).
3. (a) Dagani, R. *Chem. Eng. News* **1999**, *77*(27), 30-32. (b) McCoy, M. *Chem. Eng. News* **1999**, *77*(5), 18-19.
4. (a) McDonald, J. G.; Hites, R. A. *Anal. Chem.*, **2000**, *72*, 4859-4864. (b) Zhang, Q.; Chuang, K. T. *Environ. Sci. Technol.* **1999**, *33*, 3641-3644. (c) Zheng, Y.; Allen, D. G. *Environ. Sci. Technol.* **1996**, *30*, 1890-1895.
5. Wagner, G. W.; Yang, Y.-C. Universal decontaminating solution for chemical warfare agents. U.S. Patent 6,245,957, 2001.
6. (a) Epstein, J.; Demek, M. M.; Rosenblatt, D. H. *J. Org. Chem.* **1956**, *21*, 796-797. (b) Larsson, L. *Acta Chem. Scand*., **1958**, *12*, 723-730.
7. (a) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Bunton, C. A. *J. Org. Chem*. **1993**, *58*, 6964-6965. (b) Yang, Y.-C.; Berg, F. J.; Szafraniec, L. L.; Beaudry, W. T.; Bunton, C. A.; Kumar, A. *J. Chem. Soc., Perkin Trans. 2* **1997**, 607-613.
8. Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K. *J. Am. Chem. Soc.* **1990**, *112*, 6621-6627.
9. Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Davis, F. A. *J. Org. Chem.* **1990**, *55*, 3664-3666.
10. Marshall, E. K., Jr.; Williams, J. W. *J. Pharmacol. Exp. Therapeutics* **1921**, *16*, 259-272.
11. Lawson, W. E.; Reid, E. E. *J. Am. Chem. Soc*. **1925**, *47*, 2821-2836.
12. Anslow, W. P., Jr.; Karnofsky, D. A.; Val Jager, B.; Smith, H. W. *J. Pharmacol. Exp. Therapeutics* **1948**, *93*, 1-9.
13. (a) Drago, R. S.; Frank, K. M.; Wagner, G. W.; Yang, Y.-C. In the *Proceedings of the 1997 ERDEC Scientific Conference on Chemical and Biological Defense Research, ERDEC-SP-063*; U.S. Army Edgewood Research, Development and Engineering Center, 1998, pp. 341-342. (b) Wagner, G. W.; Yang, Y.-C. In the *Proceedings of the 1998 ERDEC Scientific Conference on Chemical and Biological Defense Research, ERDEC-SP-004*; U.S. Army Edgewood Research, Development and Engineering Center, 1999, pp. 285-291.
14. (a) Richardson, D. E.; Yao, H.; Xu, C.; Drago, R. S.; Frank, K. M.; Wagner, G. W.; Yang, Y.-C. In the *Proceedings of the 1998 ERDEC Scientific Conference on Chemical and Biological Defense Research, ERDEC-SP-004*; U.S. Army Edgewood Research, Development and Engineering Center, 1999, pp. 293-299. (b) Richardson, D. E.; Yao, H.; Frank, K. M.; Bennett, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 1729-1739.
15. Aubry, J.-M.; Bouttemy, S. *J. Am. Chem. Soc.* **1997**, *119*, 5286-5294.
16. Wagner, G. W.; Procell, L. R.; Yang, Y.-C.; Bunton, C. A. *Langmuir* **2001**, *17*, 4809-4811.